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(71) Applicant(s)
Dr Joseph Franks
2 Brookfield Avenue, Ealing, LONDON, W5 1LA, United Kingdom

(72) Inventor(s)
Dr Joseph Franks

(74) Agent and/or Address for Service
Williams,Powell & Associates
34 Tavistock Street, LONDON, WC2E 7PB, United Kingdom

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ONLINE : WPI, CLAIMS

(54) Diamond coated polymer devices for biomedical applications

(57) Improved polymer devices for biomedical applications such as catheters and other tubular inserts, breast implants and other biomedical devices are rendered biocompatible, smooth and easy to insert, non-irritant, less liable to encrustation, and less permeable by being coated with a DLC - diamond-like carbon - film, being chemically and/or physically bonded to the external surfaces of the devices by plasma assisted chemical vapour deposition system in which the DLC is deposited on to the polymer substrate in a vacuum reaction chamber using an RF supply typically at a frequency of 13.56 MHz. Alternatively the coating may be applied by sputtering a carbon target with energetic ions including argon ions by a dual ion beam or magnetron or ion enhanced deposition system; or by use of a hydrocarbon ionising beam source system. The substrate may be formed from polyurethane, latex, or silicone rubber. The DLC coating may be rendered conducting to allow an electrical potential to be applied to the coating to prevent bacterial colonisation on the catheter or other device surface, by incorporating a metal in the DLC coating by introducing a metal into the plasma from an evaporation source, sputtering source or other suitable metal source. Alternatively, a conducting film may be deposited on the polymer surface which is subsequently coated with DLC.

Apparatus for coating a polymer with DLC is also disclosed and this comprises a housing 3 containing at least one cathode 2, a support means for the substrate near to the cathode, an electrical source connectable to the cathode, means for introducing into the housing a plasma including carbon ions 4, and control means for controlling the voltage applied to the cathode(s).

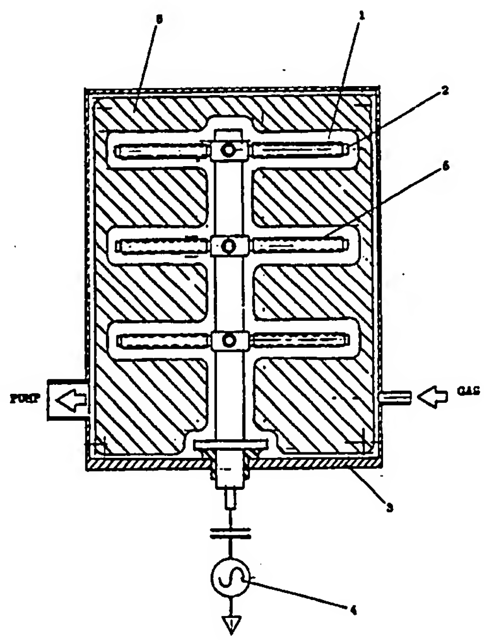

FIG. 1

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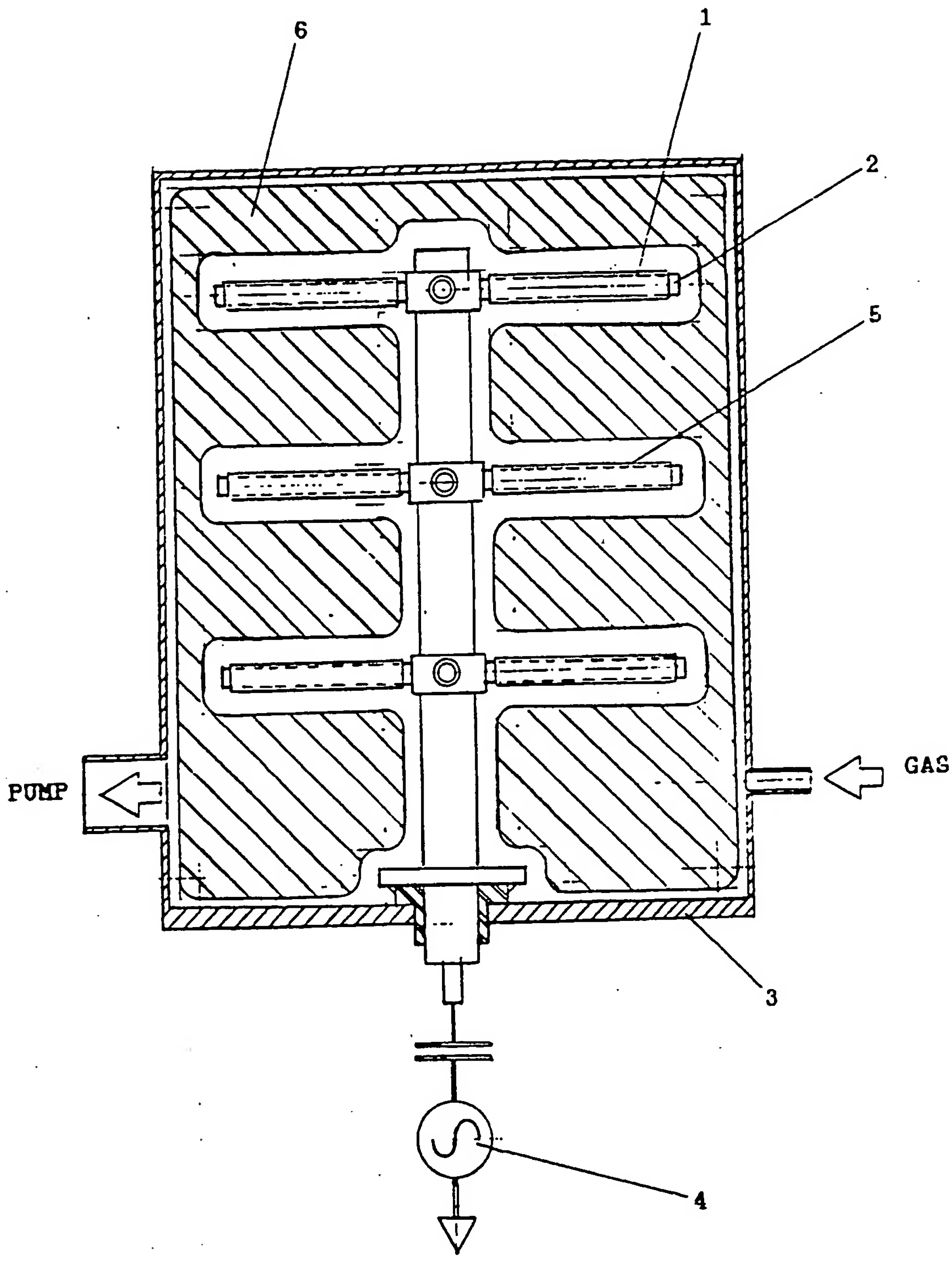

FIG.1

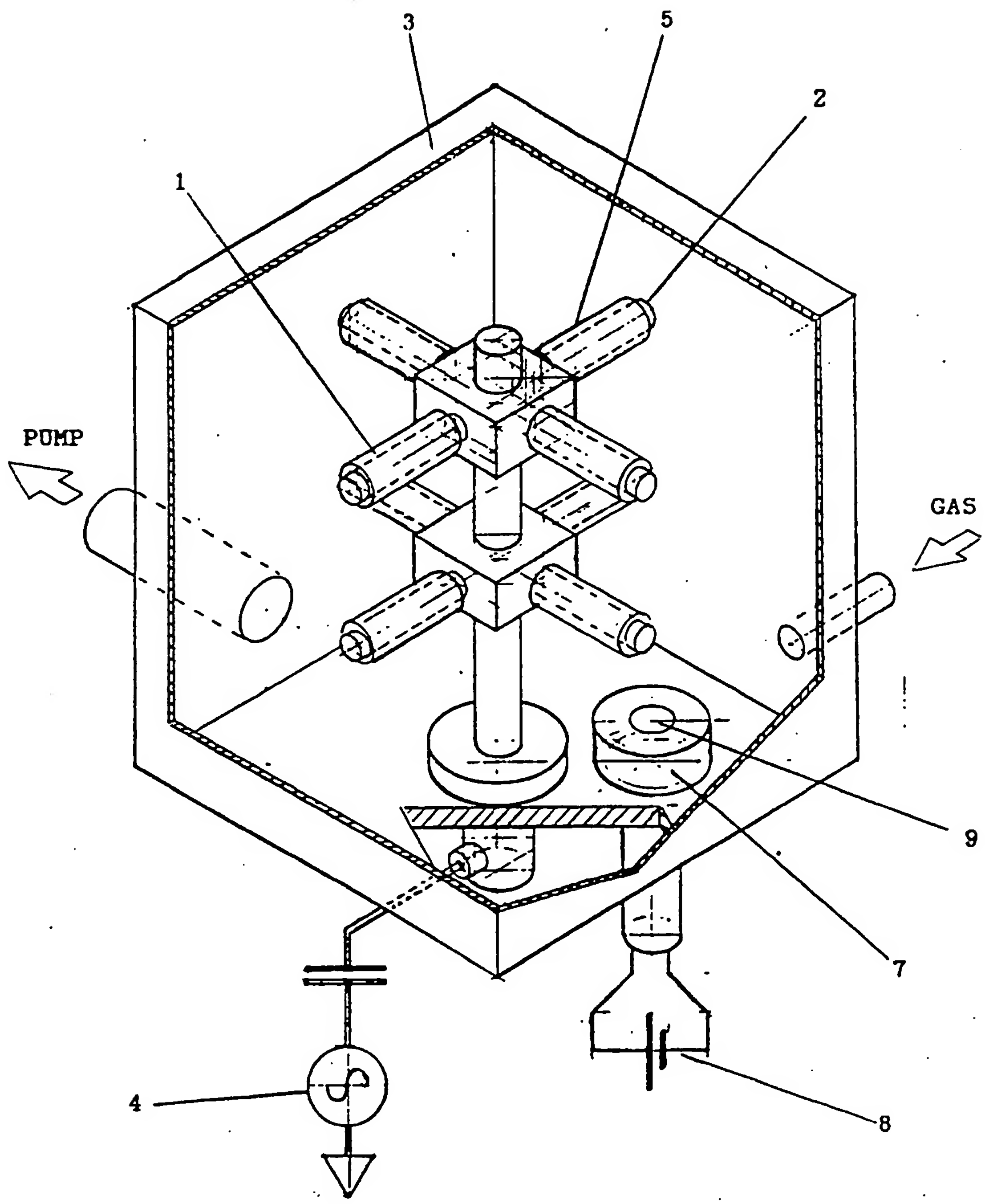

FIG.2

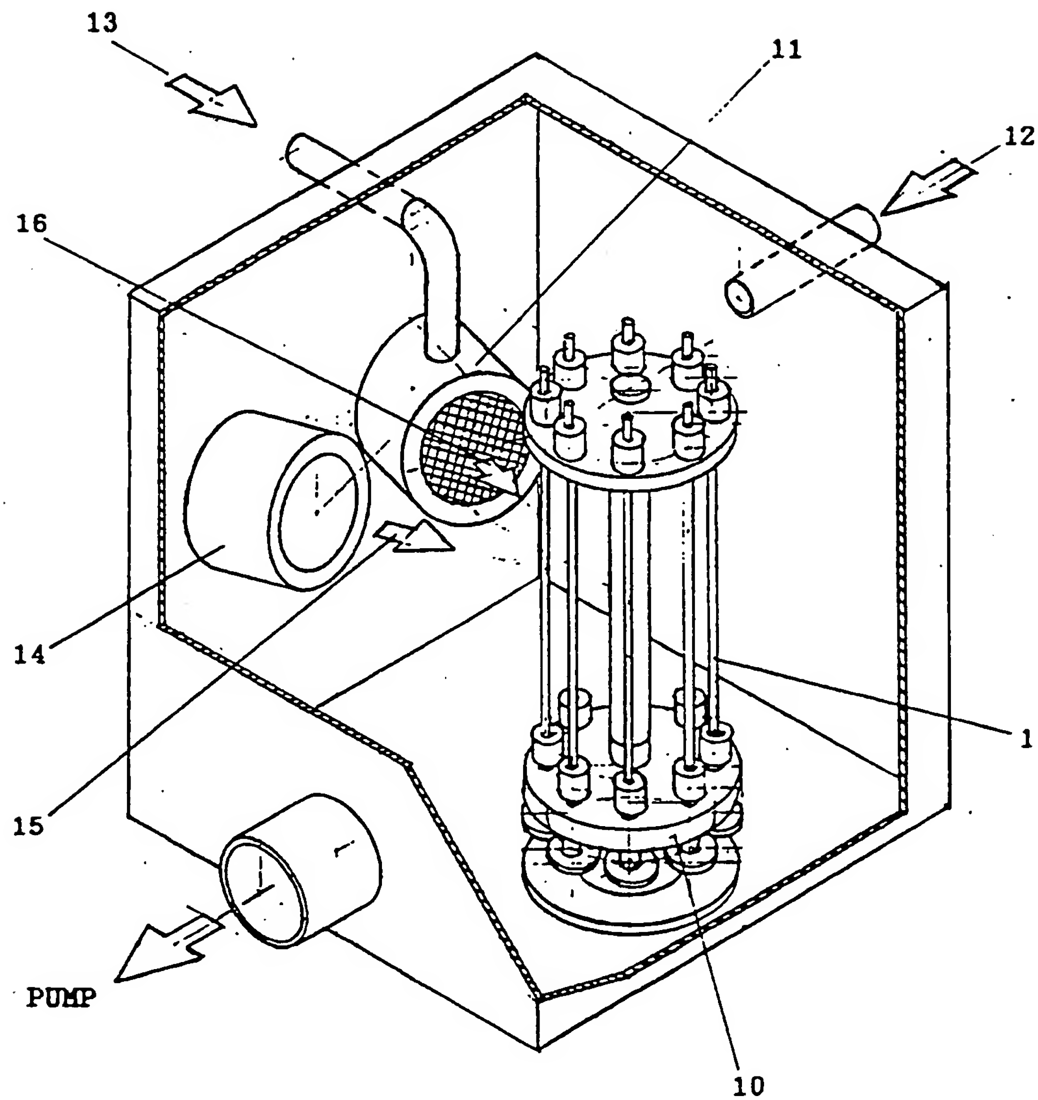

FIG.3

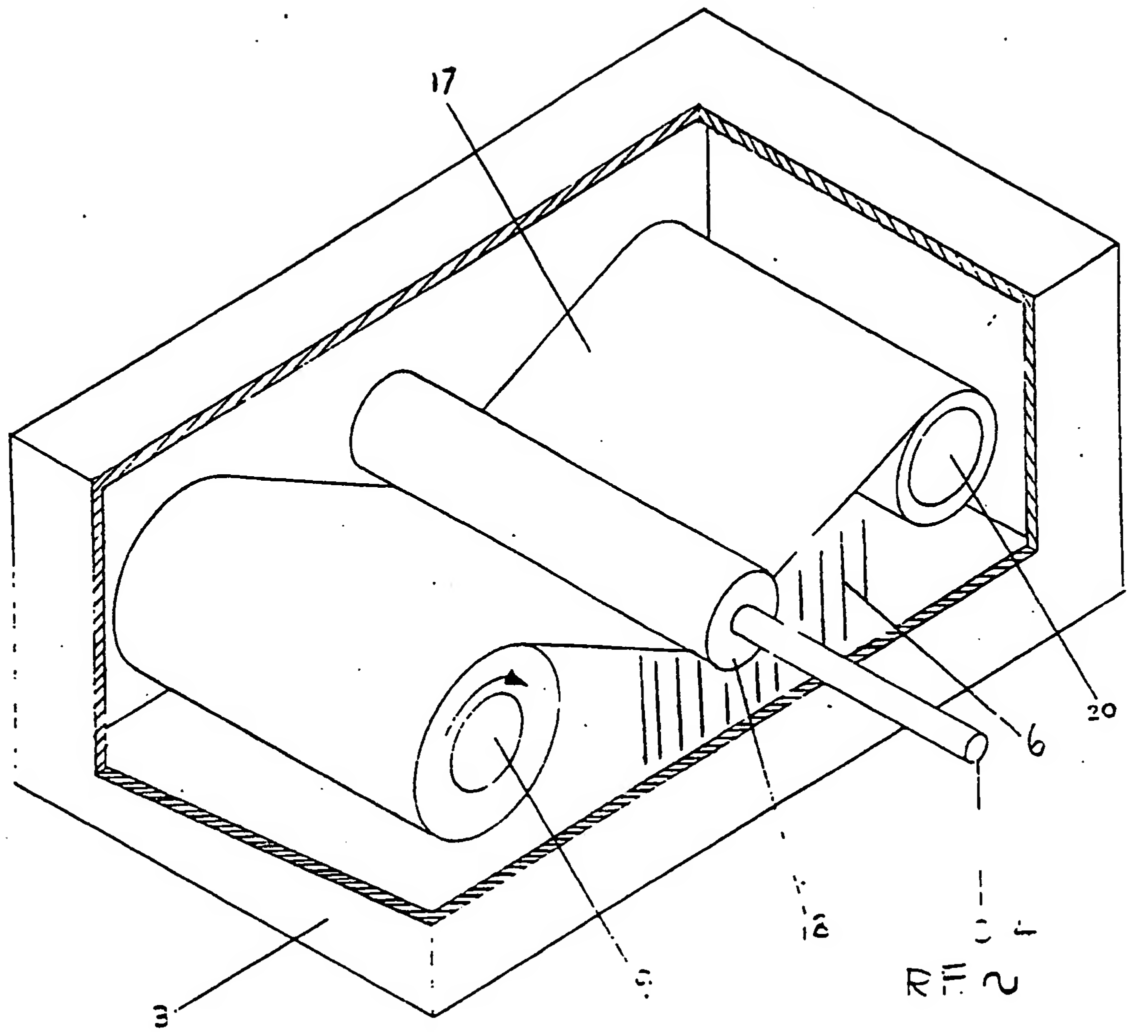

Fig 4

COATED POLYMER DEVICES FOR BIOMEDICAL APPLICATIONS

This invention relates to polymer devices insertable into the body either briefly or retained for long periods and to the coating of such inserts.

Polymer devices for biomedical applications include catheters and other polymer tube inserts, breast implants and other devices. Catheters generally provide a means of introducing fluids into the body or removing fluids from the body. Depending on application, catheters may range in diameter from less than 2mm to over 1cm. Problems which may be encountered include frictional damage during insertion, irritant effects, encrustation on urinary catheters and general deleterious effects on the biological environment in longer term treatments due to bio-incompatibility of the catheter surface. Considerations applying to catheters for conveying fluids also apply to other flexible polymer tube inserts such as those carrying heart pacemaker leads.

Problems related to breast implants are bio-incompatibility of the capsule and the diffusion and leakage of the contents of the capsule into the surrounding tissue causing adverse reactions.

The present invention seeks to provide improved polymer devices for biomedical applications.

According to an aspect of the present invention, there is provided a polymer insert for use in biomedical applications comprising a polymer substrate and a diamond-like carbon coating on the substrate. The diamond-like coating, by virtue of its composition, is less likely to cause incompatibility problems when applied to biomedical inserts.

Preferably, the polymer substrate is flexible. There has never been any attempt to apply a diamond-like coating to a flexible medical implant. However, by the methods and apparatus described herein, it has been found possible to provide a coating with satisfactory qualities.

The diamond-like coating preferably includes a metal so as to be conductive. This is particularly useful for preventing colonisation of the implant by bacteria, achieved by applying a negative electrical potential to the implant.

The substrate is preferably formed from polyurethane, latex, silactic, silicone rubber or other material having similar properties. It has been found that these materials have the required physical properties for an implant, for example flexibility, and can support a diamond-like coating.

Preferably, the diamond-like coating is chemically and/or physically bonded to the substrate by sputtering of a carbon target with energetic ions including argon ions by a dual ion beam or magnetron or ion enhanced deposition system, or a hydrocarbon ionising beam source system or, by the preferred embodiment, a plasma assisted chemical vapour deposition system.

The polymer insert may be a catheter or other tubular insert or a breast implant or other flexible implant. Examples of coated catheter include endo-tracheal catheters, intravenous catheters, suction catheters, urinary catheters, heart pacemaker lead tubes and the like. The coating can render such catheters and other implants bio-compatible, smooth and easy to insert, non-irritant and less liable to encrustation (especially in the case of urinary catheters). The diamond-like coating is also less permeable, which is very important in the case of breast implants.

According to another aspect of the present invention, there is provided apparatus

for coating a polymer substrate with a diamond-like coating comprising a housing, at least one cathode in the housing, support means for supporting a polymer substrate by the cathode, an electrical source connectable to the cathode, means for introducing into the housing a plasma including carbon ions, and control means for controlling the voltage applied to the cathode or cathodes during the coating process so produce a diamond-like carbon coating.

It has been found that with apparatus of this design, it is possible to provide a strong coating on polymer substrates, which has not been possible in the prior art.

Preferably, the introducing means includes a vapour source for introducing into the housing a vapour plasma including carbon ions. Deposition by an ion plasma has been found to be particularly effective for the coatings and substrates contemplated, in particular since it provides an enveloping coating process instead of a directional coating process as with some of the other methods.

The plasma may be any carbon containing gas, although acetylene is presently preferred.

The apparatus preferably includes a vacuum source operative to generate a vacuum of approximately 10^{-5} mbar and/or a frequency source for generating within the housing ionisation waves of radio frequency, for example approximately 13.56 MHz. It has been found that these deposition conditions produce a strong coating.

The apparatus may comprise a conductive support from which a plurality of cathodes extend, each cathode being operative to support a respective substrate for coating. The support may comprise an elongate conductive member from which a plurality of cathodes extend substantially at right angles to the axis of the support member. Alternatively, the support may include first and second support members

between which each of a plurality of cathodes extend and means for coupling electrically the first and second support members to the voltage source. These designs of apparatus are ideal for coating catheters and the like.

Alternatively, the apparatus may include spaced feed and take-up spools for feeding substrate to be coated, the cathode being disposed between the spools and having a longitudinal axis thereof substantially perpendicular to the axis of movement of substrate between the spools, the plasma source being disposed adjacent the cathode and in use hidden by the cathode by substrate to be coated. This is particularly useful for coating sheets of polymer substrate for use, for example, in producing breast implants.

According to another aspect of the present invention, there is provided a method of coating a polymer substrate by means of apparatus as herein specified comprising the steps of providing at least part of the substrate to be coated in the housing, providing a plasma containing carbon ions in the housing, energising the cathode or cathodes at a negative voltage potential and controlling the voltage potential of the cathode so as to create a diamond-like coating on the substrate.

Preferably, the method comprises the step of making the coated polymer substrate electrically conductive, for example by using plasma which contains a metal or by applying a metal layer to the polymer substrate prior to coating the substrate with carbon.

It is thus possible to reduce or overcome problems experienced with present catheters and other tubular inserts, by providing the inserts with a smooth, low friction, biocompatible coating of diamond-like carbon (DLC). DLC forms a wear and corrosion resistant, flexible and biocompatible coating. It provides a surface which reduces urine encrustation. It has been shown that a negative electrical

potential at the surface of a catheter or other tubular insert prevents colonisation by bacteria. Conductivity of the DLC coating can be increased, when required, by incorporating a suitable metal in the DLC coating or coating the polymer with a conducting film on which DLC is subsequently deposited.

Breast implants can also be coated with DLC to improve the biocompatibility of the capsule and to inhibit diffusion or leakage of the contents of the capsule into the surrounding tissue. DLC has a high atomic number density and therefore acts as a very effective diffusion barrier.

Specific embodiments of the invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is a diagrammatic representation of a plasma assisted chemical vapour deposition system for DLC coating in which catheters or other tubular inserts 1 are mounted on a cathode 2 and surrounded by a plasma 6.

Figure 2 is an isometric projection of a system as in Figure 1 in which a source 7 for incorporating a metal in the DLC coating is included.

Figure 3 is a diagrammatic representation of a DLC beam coating system in which catheters or other tubular inserts 1 are mounted on a rotating planetary holder 10.

Figure 4 is a diagrammatic representation of a plasma assisted chemical vapour deposition system in which a polymer sheet 17 passes over a cylindrical cathode 18 adjacent to the plasma 6. The coated sheet may be used to construct breast implant capsules or other biomedical devices.

It is to be understood that any component or process values specified herein may

be extended or otherwise altered without losing the effects sought, as will be readily appreciated by the skilled person.

Referring to Figure 1, catheters or other tubular inserts 1 are mounted on cathode rods 2 in a vacuum chamber 3, which is evacuated to a pressure of e.g. 10^{-5} mbar. A carbon containing gas such as acetylene, which may be mixed with other gases such as argon, is introduced into the chamber at a pressure preferably in the range 10^{-3} - 10^{-1} mbar and ionised by a radio frequency source 4 operating at e.g. 13.56 MHz, capacitively coupled to the cathode. Depending on electrode geometry and RF power, the cathode will assume a negative potential for a net zero current to flow during a cycle so that the current due to the positive charges carried by the low mobility ions during the greater part of the cycle is equal in magnitude to the negative current due to the electrons. Preferably electrode geometry and operating conditions are chosen such that the cathode potential exceeds about 150 Volts negative. Under the energetic ion bombardment, the deposited carbon 5 from the plasma 6 is bonded preferentially as diamond (sp^3).

The diameter of the cathode rods 2 should preferably be close to the internal diameter of the catheters or other tubular inserts so that most of the cathode dark space surrounding a rod is formed between the edge of the plasma 6 and the other surface of the catheter or other tubular insert 1. Depending on the diameter of the inserts, the spacing between the cathode rods 2 should be such that the dark spaces between rods do not interact.

Referring to Figure 2, a means is shown of incorporating a metal into the DLC coating 5 from a source 7 containing a metal 9 energised by a supply 8, in cases where the coating should be conductive. The metal such a tantalum may be introduced into the plasma by sputtering, evaporation or other means known to the art. The metal is co-deposited from the plasma with the carbon to render the DLC

coating conductive.

Although deposition of DLC on catheters or other tubular inserts by plasma assisted chemical vapour deposition is preferred (in part because the need for manipulating the components inside the chamber during the coating process is avoided, in part because the deposition system can readily be scaled), other methods of depositing DLC can be used. Such methods included laser ablation, dual ion beam sputtering, unbalanced magnetron sputtering or other means of DLC deposition known in the art.

The preferred method is shown in Figure 3, in which a number of catheters or other tubular inserts 1 are mounted on a rotating planetary holder 10 and coated by beam deposition 16 from an ionising source 11 fed by a gas supply 13, the gas being a carbon containing gas such as acetylene which may be mixed with other gases. Other materials, including a metal such as tantalum, may be incorporated into the DLC coating from beam 15 generated by source 14, e.g. a magnetron with a sputtering atmosphere e.g. of argon from a gas supply 12.

Other medical polymer devices may be constructed from polymer sheet. Referring to Figure 4, such sheet may be coated with DLC by passing the sheet 17 over a cathode cylinder 18 connected capacitively to a radio frequency source 4 from a pay out reel 19 to a take up reel 20. The reels may be mounted within the vacuum chamber 3 or outside the chamber, in which case the sheet enters and leaves the chamber through entrance and exit locks (not shown). The electrode geometry and operating conditions are chosen such that the cathode potential exceeds about 150 Volts negative. The plasma assisted method of coating is preferred, because the deposition system may readily be scaled up, but other methods, well known in the art, may be used for depositing DLC. The coated polymer sheet may be used to construct biocompatible low permeability devices such as breast implants.

Apparatus features not shown in Figure 4 are analagous to those shown and described with reference to the embodiments of Figures 1 to 3.

It will thus be appreciated that the coating can be applied to improve polymer devices for biomedical applications for brief or long term insertion in the body. Such devices include catheters and other tubular inserts in a variety of sizes, shapes and functions, including endotracheal catheters, intravenous catheters, suction catheters, urinary catheters and heart pace maker tubes. The exposed surfaces of the said catheters and tubes are rendered biocompatible, smooth and easy to insert and non-irritant and the surfaces of urinary catheters are less liable to encrustation. The coating may be applied by the described methods to substrate materials such as polyurethane, latex, silastic or other non-metallic material.

Other devices may be constructed from sheet, for example to produce silicone rubber capsules for breast implants. The exposed surfaces of the implants are rendered biocompatible and inhibit diffusion of the contents of the capsule such as silicone gel or saline solution.

Similarly, the external exposed surface of the catheters and other tubes, capsules and other devices can be coated with a DLC - diamond-like carbon - film, the DLC film being chemically and/or physically bonded to the surface of the substrate material by techniques such as sputtering of a carbon target with energetic ions including argon ions, using a dual ion beam deposition system, or a magnetron deposition system, or a hydrocarbon ionising beam source system, or an ion beam enhanced deposition system, or alternatively and preferably a plasma assisted chemical vapour deposition system. In this the DLC is deposited on to the substrate from a plasma produced by ionising a carbon containing gas including acetylene in a vacuum reaction chamber using an RF supply typically at a frequency of 13.56 MHz.

The DLC coating may also be rendered conducting by incorporating a metal in the DLC coating by introducing a metal into the plasma from an evaporation source, sputtering source or other suitable metal source. This can allow an electrical potential to be applied to the said coating to prevent bacterial colonisation on the catheter or other tube surface. Alternatively a conducting film may be applied to the polymer surface which is subsequently coated with DLC.

During manufacture a plurality of the said catheters and other tubular inserts may be fitted on to a purpose made cathode to ensure simultaneous multiple DLC coating of the said catheters and other tubular inserts. On an industrial scale polymer sheet may be coated with the pay out and take up reels outside the vacuum chamber.

The disclosures in British patent application no. 94/05029.1, from which this application claims priority, and in the abstract accompanying this application are incorporated herein by reference.

Claims:

1. A polymer insert for use in biomedical applications comprising a polymer substrate and a diamond-like carbon coating on the substrate.

2. A polymer insert according to claim 1, wherein the polymer substrate is flexible.

3. A polymer insert according to claim 1 or 2, wherein the diamond-like coating includes a metal so as to be conductive.

4. A polymer insert according to claim 1, 2 or 3, wherein the substrate is formed from polyurethane, latex, silactic, silicone rubber or other material having similar properties.

5. A polymer insert according to any preceding claim, wherein the diamond-like coating is chemically and/or physically bonded to the substrate by sputtering of a carbon target with energetic ions including argon ions by a dual ion beam or magnetron or ion enhanced deposition system, or a hydrocarbon ionising beam source system or a plasma assisted chemical vapour deposition system.

6. A polymer insert according to any preceding claim, wherein the polymer insert is a catheter or other tubular insert or a breast implant or other flexible implant.

7. Apparatus for coating a polymer substrate with a diamond-like coating comprising a housing, at least one cathode in the housing, support means for supporting a polymer substrate by the cathode, an electrical source connectable to the cathode, means for introducing into the housing a plasma including carbon ions, and control means for controlling the voltage applied to the cathode or cathodes

during the coating process so produce a diamond-like carbon coating.

8. Apparatus according to claim 7, wherein the introducing means includes a vapour source for introducing into the housing a vapour plasma including carbon ions.

9. Apparatus according to claim 7 or 8, comprising a vacuum source for creating a vacuum within the housing.

10. Apparatus according to claim 9, wherein the vacuum source is operative to generate a vacuum of approximately 10^{-5} mbar.

11. Apparatus according to any one of claims 7 to 10, comprising a frequency source for generating within the housing ionisation waves of radio frequency.

12. Apparatus according to claim 11, wherein the frequency is approximately 13.56 MHz.

13. Apparatus according to any one of claims 7 to 12, comprising a conductive support from which a plurality of cathodes extend, each cathode being operative to support a respective substrate for coating.

14. Apparatus according to claim 13, wherein the support comprises an elongate conductive member from which a plurality of cathodes extend substantially at right angles to the axis of the support member.

15. Apparatus according to claim 13, wherein the support includes first and second support members between which each of a plurality of cathodes extend and means for coupling electrically the first and second support members to the voltage source.

16. Apparatus according to any one of claims 7 to 12, comprising spaced feed and take-up spools for feeding substrate to be coated, the cathode being disposed between the spools and having a longitudinal axis thereof substantially perpendicular to the axis of movement of substrate between the spools, the plasma source being disposed adjacent the cathode and in use hidden from the cathode by substrate to be coated.

17. Apparatus according to any one of claims 7 to 16, comprising means to introduce into the plasma a metal.

18. Apparatus according to claim 17, wherein the introduction means comprises an evaporation source, sputtering source or other suitable metal source.

19. A method of coating a polymer substrate by means of apparatus according to any one of claims 7 to 18, comprising the steps of providing at least part of the substrate to be coated in the housing, providing a plasma containing carbon ions in the housing, energising the cathode or cathodes at a negative voltage potential and controlling the voltage potential of the cathode so as to create a diamond-like coating on the substrate.

20. A method according to claim 19, comprising the step of generating radio frequency ionisation energy in the housing so as to ionise carbon atoms contained in plasma in the housing.

21. A method according to claim 20, wherein the ionisation energy is generated at a frequency of approximately 13.56 MHz.

22. A method according to claim 19, 20 or 21, comprising the step of creating a vacuum in the housing.

23. A method according to claim 22, comprising the step of creating a vacuum of approximately 10^{-5} mbar.

24. A method according to any one of claims 19 to 23, comprising the step of making the coated polymer substrate electrically conductive.

25. A method according to claim 24, wherein the plasma contains a metal.

26. A method according to claim 24, wherein a metal layer is applied to the polymer substrate prior to coating the substrate with carbon.

27. A polymer insert for use in biomedical applications substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

28. Apparatus for coating a polymer substrate with a diamond-like coating substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

29. A method of coating a polymer substrate substantially as hereinbefore described with reference to the accompanying drawings.

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Patents Act 1977 Examiner's report to the Comptroller under Section 17 (The Search report)	Application number GB 9505194.2
Relevant Technical Fields (i) UK Cl (Ed.N) C7F (FHB, FHE, FHX, FPCX, FPDX, FPEX, FCSX, FCVX); A5R (RCG, RAG, RAP) (ii) Int Cl (Ed.6) C23C (14/06, 16/26); A61L (27/00, 29/00)	Search Examiner P G BEDDOE Date of completion of Search 22 MAY 1995
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE: WPI, CLAIMS	Documents considered relevant following a search in respect of Claims :- 1-6, 27

Categories of documents

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Category	Identity of document and relevant passages		Relevant to claim(s)
X	EP 0580094 A1	(BECTON) see especially Claim 1; columns 3-6	1, 4, 5
X	EP 0440326 A1	(BAUSCH) see especially column 5 lines 50-51; Claim 1	1, 4, 5
X	EP 0302717 A1	(ION TECH) see especially column 1 lines 27-38; column 2 lines 9-19	1, 4-6
X	EP 0278480 A2	(SEMICONDUCTOR) see especially column 2 lines 51-55; column 4 lines 27-35	1, 4, 5
X	EP 0224080 A2	(SORIN) see especially page 5 lines 16-22, lines 42-49 (2nd column)	1, 4-6
X	EP 0102328 A2	(SORIN) see especially page 5 lines 20-23, Claim 2	1, 4-6
X	US 5133845	(SORIN) see especially column 5 line 35 - column 6 line 20	1, 4-6
X	US 5133757	(SPIRE) see especially column 3 line 50 - column 4 line 10	1, 2, 4-6
X	US 5055318	(BEAMALLOY) see especially column 5 lines 9-13; Example 1	1, 4, 5
X	US 4537791	(CORDIS) see especially column 2 line 35 - column 6 line 20	1, 4-6

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Continuation page

Category	Identity of document and relevant passages	Relevant to claim(s)
X	US 4490229 (MIRTICH) see especially column 1 lines 19-25; column 4 lines 4-9	1, 4, 5
X	US Patent Application 7-502121 (BERGER) see examples	1, 2, 4, 5
X	WPI Accession No 91-204818/28 and JP 3130363 A (NIKON) see abstract	1, 2, 4, 5